

Zooming-in on the charge ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$

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We report direct evidence of charge/orbital ordering of low energy electronic states of Cu in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ortho-II phase in both the CuO_3 chain and the CuO_2 plane. Huge enhancement of the $(\frac{1}{2}, 0, 0)$ superstructure Bragg peak is observed when photon energy is tuned to the $\text{Cu } L_{2,3}$ absorption edge with large polarization dependence. The ordering in the CuO_2 plane discovered here sheds new light on how the one dimensional $\text{Cu} - \text{O}$ chains affect the CuO_2 plane, and why many normal and superconducting state properties of this system exhibit strong anisotropy.

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$\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is one of the most studied high temperature cuprate superconductors. Many important observations, such as the neutron resonance mode[1] and d-wave superfluid behavior,[2] were first made on this system. However, whether the detailed properties of these phenomena are generic to all cuprates still remains questionable due to the presence of CuO_3 chains in addition to CuO_2 planes in this material. So far, virtually all known experimental methods have been used to study this system, but little is known about the role that CuO_3 chains play in the low energy electronic structure, or if the chain is superconducting or even conducting at all. For example, surface reconstruction of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ prevents angle resolved photoemission spectroscopy or scanning tunnelling spectroscopy from obtaining reliable electronic structure information.

The Ortho-II chain-ordered phase of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ is an ideal system for studying the local interplay between the chain and the plane. Conventional x-ray scattering experiments on this system exhibit a superlattice Bragg peak corresponding to a doubling of the unit cell. The doubling is modelled with oxygen atoms in the CuO_3 chain layers being ordered into alternating full and empty chains, as illustrated in Fig. 1a. [3, 4, 5] If the chain does affect the plane, one would expect charge ordering in the plane induced by this chain ordering, and by studying its nature, one can study how the electronic structure and the superconductivity in the CuO_2 plane are affected. However, in practice, this is a difficult task because besides the primary order, i.e. alternate filling of oxygen accompanied by alternation in the valence states of chain Cu 's, there are additional structural orders of the Y and Ba heavy ions. These ions are located between chains, and chain ordering changes their positions. Since all the electrons in the system contribute to conventional x-ray scattering with large contributions from heavy atoms, the

primary order is not directly studied in such experiments. That the chain ordering causes these changes in position is a plausible speculation, but the proposed model of oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ presented in Fig. 1a and especially the accompanying change in Cu oxidation states remains to be verified through more direct experiments.

We applied resonant soft x-ray scattering to this problem, which is a novel diffraction technique that can provide element specific and spatial information of the valence electron distribution.[6, 7] We found that the valence state of the chain Cu is ordered, moreover, this ordering induces significant charge and orbital ordering in the plane. This 1D footprint of the chain on the plane gives a plausible explanation for many of the observed unusual phenomena in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$.

The Resonant soft x-ray scattering (RSXS) experiments were performed on untwinned ortho-II phase $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ single crystal at the soft x-ray Beamline X1-B of National Synchrotron Light Source (NSLS), using the "Spinoza diffractometer" in an ultra-high-vacuum (UHV) chamber with a base pressure of $2 \times 10^{-10} \text{ mbar}$ as described in ref.[7]. UHV is needed because of the surface sensitivity of the technique, as the x-ray penetration depth in this experiment is about 1200 \AA . The sample was prepared as described in ref.[5] with a superconducting transition temperature of 62K. Data were collected at 100K.

As illustrated in Fig. 1b, when the photon energy is tuned to the $\text{Cu } 2p \rightarrow 3d$ transition, the contribution from Cu atoms to the scattering is greatly enhanced through a virtual excitation process called resonant or anomalous scattering[6]. In the dipole approximation, it is described by the atomic form factor:

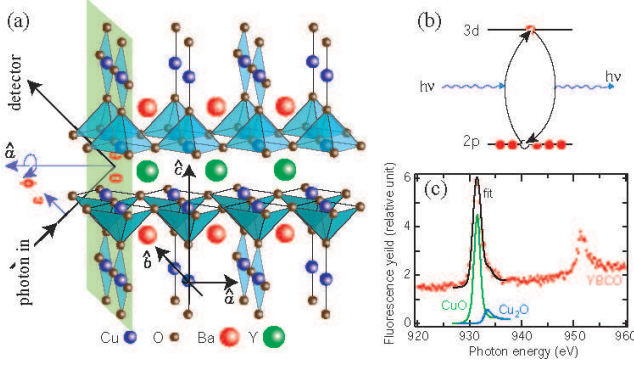


FIG. 1: The system under study and the experimental setup. (a) illustrates the proposed ortho-II ordered phase of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$. The chain filled with oxygen (full chain) and the one without oxygen (empty chain) correspond to Cu^{2+} and Cu^{1+} respectively. The $\theta/2\theta$ Bragg scattering experimental geometry is also shown, with photon polarization ε in the $\theta/2\theta$ plane. The sample can be rotated azimuthally around the crystalline \hat{a} -axis without breaking the Bragg condition. The azimuthal angle is defined to be 0° in the geometry shown, where the $\theta/2\theta$ plane and the ac plane coincide. (b) The $\text{Cu } 2p \rightarrow 3d$ resonant scattering process which dramatically enhances the scattering from $\text{Cu } 3d$ orbitals. (c) Fluorescence yield XAS spectrum for $\text{Cu } 2p$ to $3d$ transitions in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$, which can be fitted by a linear combination of CuO and Cu_2O XAS spectra taken from ref.[8].

$$f \propto \sum_f \left| \sum_m \frac{\langle \psi_f, \omega_1 | \varepsilon \cdot \mathbf{r} | \psi_m \rangle \langle \psi_m | \varepsilon' \cdot \mathbf{r} | \psi_i, \omega_0 \rangle}{E_m - E_i - \hbar\omega_0 - i\Gamma_m} \right| \cdot \delta(E_f + \hbar\omega_1 - E_i - \hbar\omega_0)$$

where ψ_i , ψ_m , and ψ_f are the initial, intermediate, and final state wavefunctions with energies of E_i , E_m , and E_f respectively. Γ_m is the life time energy broadening of the intermediate state. ω_0 and ω_1 are the incoming and scattered photons with polarization ε and ε' respectively. Apparently, the scattering signal contains information of electronic structure of the states involved. In this case, if ψ_i contains $3d$ holes, $\text{Cu } 2p \rightarrow 3d$ transition is allowed to the state ψ_m , and therefore the $\text{Cu } 3d$ states and their spatial distribution are probed directly. On the contrary, ordinary resonant hard x-ray scattering based on $\text{Cu } 1s \rightarrow 4p$ transition only probes empty $4p$ states, which contribute only weakly to the low energy physics in the problem. The $\text{Cu } 2p \rightarrow 3d$ transition has been extensively studied by x-ray absorption spectroscopy (XAS), where two peaks around 930 eV and 950 eV correspond to final states with $2p_{3/2}$ and $2p_{1/2}$ core holes respectively, referred to as the $\text{Cu } L_3$ and L_2 absorption edges (Fig. 1c). The $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ L_3 edge can be fitted by a linear combination of CuO and Cu_2O spectra, consistent with the model in Fig. 1a, where Cu is in a nominally $\text{Cu}^{2+}(3d^9)$ in the full chain, and $\text{Cu}^{1+}(3d^{10})$ state in the empty

chain. Due to hybridization with oxygen, there are still some $3d$ holes on Cu^{1+} , contributing weakly to $2p \rightarrow 3d$ transition in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ at an energy $\sim 2\text{eV}$ higher than the main Cu^{2+} peak. Because the resonant scattering arises via the dipole allowed ($2p^6 3d^9 \rightarrow 2p^5 3d^{10}$) transitions, it is dominated by Cu atoms in the empty or full chains at different photon energies, resulting in a large contrast and a huge enhancement of the superlattice Bragg peak.

We will now use this contrast in the Cu^{1+} and Cu^{2+} scattering to study the ordering of $\text{Cu } 3d$ holes. Data were taken in a $\theta/2\theta$ Bragg diffraction geometry as illustrated in Fig. 1a. The scattering intensity as a function of angle and photon energy, or resonance profile, is shown in Fig. 2a. The $(1/2, 0, 0)$ Bragg peak corresponding to the Ortho-II superstructure is observed at all photon energies, with two resonances occurring near the $L_{2,3}$ absorption edges. The intensity far from the Bragg angle is very weak, which indicates that the contamination to the Bragg peak from isotropic diffuse scattering and fluorescence is negligible. Compared with the off-resonance intensity at 920 eV, the measured Bragg peak intensity is enhanced by a factor of 62 at the L_3 edge, and 8 at the L_2 edge. The weak enhancement at the L_2 is mainly caused by the competing non-radiative Coster-Kronig decay channel of the $2p_{1/2}$ core-hole.[9]

For the non-resonant scattering, the ordered O^{2-} ions in chains contribute on the order of $10^2 = 100$, while the alternating chain Cu^{2+} and Cu^{1+} ions just contribute on the order of $1^2 = 1$. As there is additional scattering from the Y^{3+} and Ba^{2+} ions, the Cu contribution to the off-resonance scattering is estimated to be less than 1%. Therefore, the Cu contribution is enhanced by more than 6200 times at the L_3 edge. Such a gigantic enhancement is rarely observed, and far beyond what one would expect if Cu ions are simply displaced from their stoichiometric position with no change in valence. [Actually, Cu ions are situated in between either two full or two empty chains, its displacement (if any) should be very small.] Therefore, this observation directly proves that the local electronic structure or electron density of the $\text{Cu } 3d$ orbitals is modulated with a period of $2a$ perpendicular to the chain in the Ortho-II phase, which should have a significant effect on the low energy electronic structure.

Having determined that the $\text{Cu } 3d$ holes are ordered, the next step is to zoom-in even further and try to distinguish the ordering of the chain Cu from that of the plane Cu . Because the holes are mainly situated in the ab plane for the plane Cu , and bc plane for the chain Cu , their contribution to the scattering cross-section will have very different polarization dependencies. Therefore, by comparing scattering intensities taken at different polarizations, one can differentiate between chain and plane $\text{Cu } 3d$ hole orbitals, and separately investigate their ordering. The polarization can be changed by using different azimuthal angles ϕ (Fig. 1a). For $\phi = 0^\circ$, and 90° , polarization

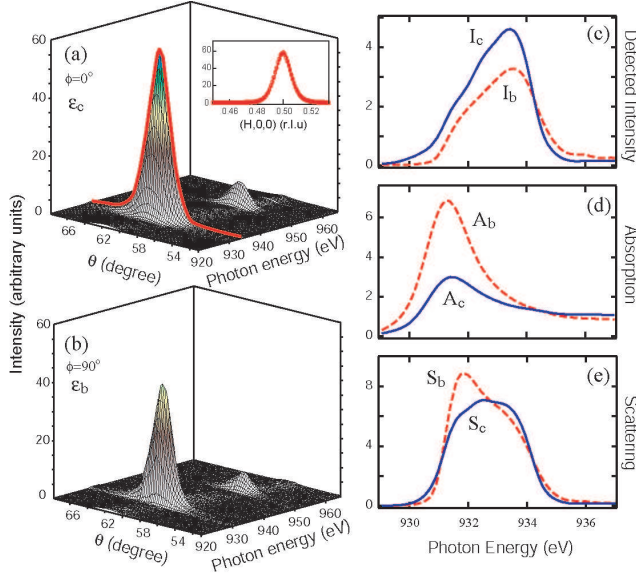


FIG. 2: Resonant soft x-ray scattering results. (a) and (b), The scattered photon intensity as a function of energy and angle for $\phi = 0^\circ$ and 90° respectively. Inset: The $(1/2, 0, 0)$ Bragg peak at resonance (i.e. the thick curve through the L_3 peak in a) in reciprocal lattice unit, which is well described by an anisotropic Lorentzian function,[3, 5] giving a coherence length of about 60\AA . (c) The integrated (over momentum) Bragg intensity; (d) the x-ray absorption; and (e), the absorption-corrected scattering as a function of the photon energy. Arbitrary units are used here.

$\varepsilon_c = \cos(\theta_B)\hat{a} + \sin(\theta_B)\hat{c}$ and $\varepsilon_b = \cos(\theta_B)\hat{a} + \sin(\theta_B)\hat{b}$ respectively (denoted by subscript c and b hereafter as the \hat{a} -component is fixed), where θ_B is the Bragg angle. Figs. 2a and 2b are the resonance profiles for the $L_{2,3}$ edge at $\phi = 0^\circ$ and 90° respectively. They are normalized at the non-resonant intensity on the low photon energy side, where the atomic form factor is basically independent of the polarization. The momentum-integrated Bragg peak intensity (I) does show significant polarization dependence as shown in Fig. 2c for the L_3 edge. As the incoming and scattered photons will be absorbed in the material, the measured data (Fig. 2c) has to be corrected for the polarization dependent self-absorption effect by $I = S/A$ where S and A are the scattering and absorption cross-sections respectively. [10] The x-ray absorption in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ has been well studied, and is shown in Fig. 2d for the two azimuthal angles.[11, 12] The absorption-corrected resonance scattering as a function of photon energy is shown in Fig. 2e, which gives the ratio of the integrated total scattering weight over the entire L_3 edge for two azimuthal angles is $\int S_c dE / \int S_b dE = 0.92 \pm 0.05$. One finds that scattering and absorption have different lineshapes here, and resonance of the scattering arises at slightly higher photon energies (about 0.5 eV) than the absorption. This is because the scattering is governed by the amplitude and absorption by the imaginary part of the atomic form factor.[10]

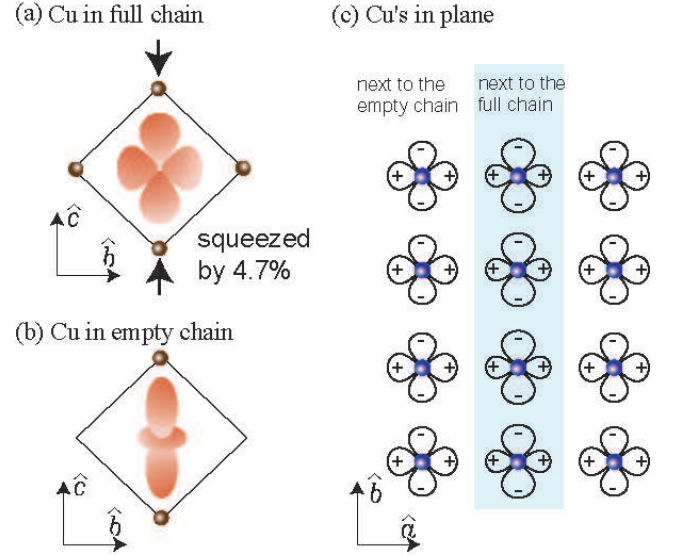


FIG. 3: Estimation of the Charge and orbital ordering in the CuO_2 plane. Cartoons of the hole wave functions in the (a) full chain and (b) empty chain. (c) is a cartoon of possible charge/orbital ordering of the holes in different planar Cu ions that can reproduce the data.

The measured weaker scattering for light partially polarized along \hat{c} than along \hat{b} cannot be understood if one assumes a homogeneous plane. As illustrated in Fig. 3a, the CuO_3 plaquet in the full chain is squeezed by about 4.7% in the \hat{c} direction. Both DFT calculations and quantum chemistry analysis show that this would cause a mixing of the chain $\text{Cu } 3d_{3x^2-r^2}$ and $3d_{y^2-z^2}$ orbitals and relocate more holes along the \hat{c} axis. In the empty chain (Fig. 3b), the $\text{O}-\text{Cu}-\text{O}$ dumbbell structure also drives a hole into the $\text{Cu } 3d_{3z^2-r^2}$ orbital, so that most of the holes are situated along the \hat{c} direction. Because the energy distribution of holes is centered at different positions for different chains as suggested by XAS data (Fig.1b), both the full and empty chain scatter \hat{c} -polarized light more than the \hat{b} -polarized light, opposite to the observation. This clearly shows that substantial charge density modulations also exist in the CuO_2 plane layer to give more scattering to the \hat{b} -polarized light.

Besides the qualitative claims that one can derive from RSXS, it is even more important that it could provide (if not pin down) some quantitative information on the local electronic structure. In the case here, the measured S_c and S_b directly relate to the occupation of the e_g orbitals of the four different types of Cu ions in the unit cell. Although it is not possible to determine these eight functions of energy based on S_c and S_b , in principle, a full determination should be possible, after further information is obtained with more experiments performed in cleaner $\sigma\sigma$ experimental geometry and at more azimuthal angles. we leave this for future studies.

This planar charge/orbital ordering is associated with many factors, including the Madelung potential of extra

O ions in the full chain which attract more holes in the planar *Cu* underneath, the long range Coulomb interaction between holes, the hybridization between the p_z orbital of the apical *O* (shared by the chain and plane) and the planar *Cu* $3d_{3z^2-r^2}$ orbital and so on. Our simple quantum chemical estimations with parameters established in experiments and numerical studies,[13] indicates that to fit the data, the charge modulation is on the order of 0.05 holes in planar *Cu* ions and accompanied by orbital modulations, *i.e.* different mixing of planar $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals at different sites as illustrated by a cartoon in Fig. 3c. Recent nuclear quadruple resonance (NQR) experiments observed four different *Cu* sites corresponding to two planar and two chain *Cu* sites.[14] We believe it is directly related to the charge/orbital ordering discussed here, as the electric field gradient at the *Cu* nucleus is very sensitive to the relative occupation of $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals since these two orbitals contribute with opposite signs to the electric field gradient.

We have shown that even if the chains are insulating, as most defected 1D system would be, they imprint their 1D nature onto the planar low lying electronic states. This charge/orbital ordering would cause noticeable effects on the superconductivity because of the high sensitivity to doping of the cuprates. Without having to include stripes as a separate physical effect,[15] the planar charge/orbital ordering discussed here might provide an alternative plausible explanation for the observed extraordinarily strong anisotropy in its superfluid density,[16] superconducting gap,[17] and conductivity,[18] which are all significantly larger for the \hat{b} direction than for the \hat{a} direction. It might also provides a preferential direction for the observed incommensurate magnetic fluctuation along \hat{a} , although we note that this magnetic fluctuation has a much larger length scale ($\sim 10a$).[19, 20]

Strongly correlated systems are known to exhibit rich structural, electronic and magnetic order, which are driven by only a few valence electrons.[21, 22] Extensive and detailed neutron and magnetic x-ray studies have revealed the magnetic correlations and order.[19, 20, 23, 24] In this paper we present the first direct studies in cuprates of what happens in the charge channel, demonstrating strong charge modulations distinct from the ordering observed in the spin channel. The spatial information of the electronic states revealed partially here sets the stage for understanding of many anomalous properties in the system. We expect more comprehensive understanding of many other strongly correlated systems will be reached with the help of RSXS.

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